Translated from *Uspekhi Khimii* **58** 1145–1174 (1989) U.D.C. 547.512

# Carbene synthesis and chemical reactions of cyclopropene-3-carboxylate esters—promising intermediates for organic synthesis

M N Protopopova, E A Shapiro
Zelinskii Institute of Organic Chemistry, USSR Academy of Sciences, Moscow

ABSTRACT. The data on the methods of synthesis and chemical reactions of cyclopropene-3-carboxylate esters have been correlated and classified. Particular attention has been given to the direct carbene synthesis of cyclopropene esters, which provides an accessible route to compounds of this series. In studying the chemical reactions particular attention has been given to selective reactions that provide the opportunity of using cyclopropene-3-carboxylate esters in organic synthesis to obtain various types of compounds.

The bibliography includes 112 references.

## Contents

I. Introduction 667
II. Synthesis of cyclopropene-3-carboxylate esters by the diazo method 667
III. Other methods for synthesising cyclopropene-3-carboxylate esters 669
IV. Chemical reactions of cyclopropene-3-carboxylate esters 669

## I. Introduction

The preparation of cyclic molecules containing three carbon atoms by the reaction of aliphatic diazo compounds with unsaturated acceptors using the diazo method and a study of their chemical reactions constitute one of the most productive trends in the use of carbene reactions in organic synthesis.

In 1956 D'yakonov[1] used the synthesis of ethyl 2-methyl-3-phenylcyclopropene-3-carboxylate to demonstrate the possibility of employing the diazo method to obtain these compounds which were very novel at that time from readily available acetylenes. At the end of the 1950s and the beginning of the 1960s a series of studies was carried out by Breslow[2–4] into the synthesis using the diazo method and an investigation of the simplest chemical properties of cyclopropene esters.

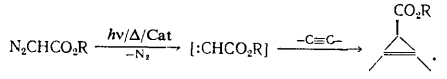
However, a systematic and detailed study of the reactions of cyclopropene-3-carboxylate esters only became feasible during the 1970s when the D'yakonov method was substantially improved by Soviet[5–7] and foreign[8] research workers, which led to cyclopropene-3-carboxylate esters becoming the most readily available class of carbofunctional cyclopropene compounds. During these years the varied reactivity of cyclopropene esters was demonstrated, which was an indication of their future potential in organic synthesis to obtain derivatives of cyclopropane, cyclopropene and cyclobutane, various furans, γ-butyrolactones and α-pyrans, and also many acyclic carbofunctional compounds.

Despite the large number of experimental studies in the literature, there are no review publications on the chemistry of cyclopropene-3-carboxylate esters. The last review on the chemistry of cyclopropene compounds[9] dates back to 1966 and contains very limited information on the properties of cyclopropene-3-carboxylate esters.

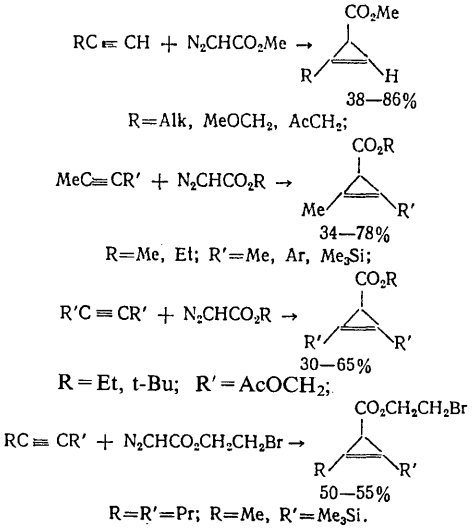
The present work is the first attempt to give a systematic account of the literature material including the studies of the present authors on the synthesis and chemical reactions of cyclopropene-3-carboxylate esters and it reflects the state of this topic at the end of 1987.

## II. Synthesis of cyclopropene-3-carboxylate esters by the diazo method

The diazo method is based on the carbene decomposition reaction of alkyl diazoacetates (ADA) that takes place on exposure to radiation, heating, or catalysts (Cat). Addition of the resulting free or complexed carbenes to triple bonds gives cyclopropene-3-carboxylate esters:[10]

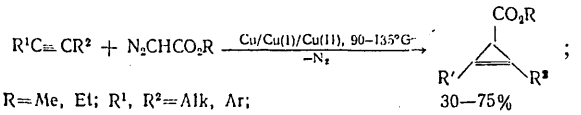


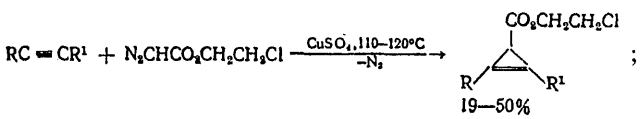
The most important preparative synthesis is the thermocatalytic method for decomposition of alkyl diazoacetates. By using rhodium compounds (for example, rhodium acetate) as catalysts for this process, it is possible to obtain cyclopropene-3-carboxylate esters in high yield even at room temperature from both terminal and internal (including those substituted with functional groups) acetylenes:[8,11–16]



In order to suppress the secondary formation of fumarate and maleate esters—formal dimers of the carbenes—the reaction is carried out with a 2.5–3-fold molar excess of acetylene.

The use of traditional copper catalysts requires a temperature of 90–140 °C for the decomposition of ADA and gives satisfactory yields of cyclopropene esters only in the case of disubstituted acetylenes which are usually employed in 2–10-fold molar excess relative to ADA:[13,17–23]

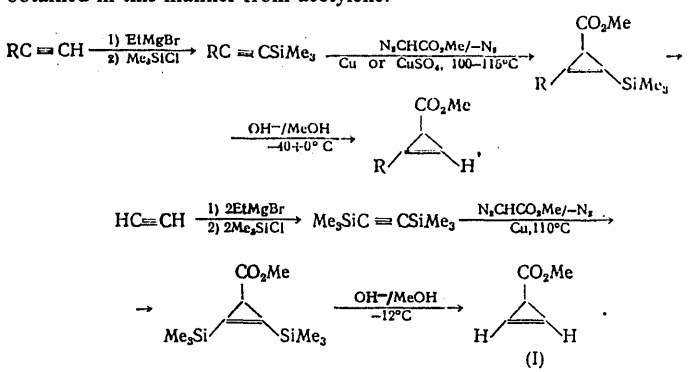



R=Pr, $R^1$=Pr, $Me_3Si$; R=cyclo-$C_3H_5$, $R^1$=$Me_3Si$.

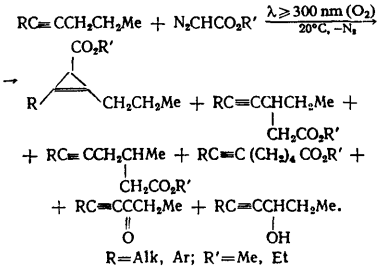
The yield of products and the selectivity of the process depend to a significant extent on the concentration of catalyst. For example, in the case of copper bronze a molar ratio of catalyst to acetylene of 0.02 : 1 is the otpimum,[22] while when using copper salts the optimum ratio is 0.001 : 1.[21]

When ADA are reacted with terminal acetylenes in the presence of copper compounds, the corresponding cyclopropene-3-carboxylate esters are formed in yields not greater than 16%.[7,24] The synthesis of such cyclopropenes can be carried out more effectively by using the so-called silyl protection method, which is based on the ready hydrolytic cleavage of the C–Si bond in trimethylsilyl-substituted cyclopropene-3-carboxylate esters.[6,25–29] In particular, the methyl ester (I) of the simplest cyclopropene-3-carboxylic acid † was obtained in this manner from acetylene.[26]




Significant disadvantages of this method are its multistage nature and the insufficiently high overall yields of cyclopropene esters (25–30%).

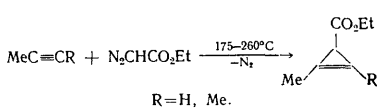
In the photolytic initiation of the reaction between acetylenes and ADA, products derived from the introduction of carbenes into the C–H bond—the corresponding esters of acetylenic acids—are formed together with cyclopropenes, while in the presence of air acetylenic ketones and alcohols are further formed. As a result the yield of cyclopropene esters from internal acetylenes does not usually exceed 40%,[11,12] only in rare cases does it reach 60%,[32] while from terminal acetylenes it is 17–20%.[22]



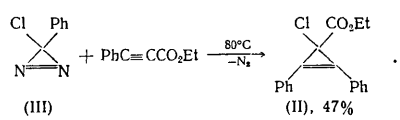

The preparation of cyclopropene-3-carboxylate esters purely by a thermal reaction between ADA and disubstituted acetylenes requires a temperature of 130 °C or above[24,31] and it is usually accompanied by destruction and oligomerisation of the initial and final products as well as by a number of other side reactions, as a result of which the yields of cyclopropene esters do not exceed 20%.[31,32]

Cyclopropene-3-carboxylate esters that are unsubstituted or monosubstituted at the double bond cannot be obtained at all under normal conditions by thermal reaction of ADA with acetylene or 1-alkynes. Acetylene and its derivatives when heated with ADA to 100 °C form only pyrazoles,[33–36] and at higher temperatures (150–200 °C) the initial and final products are almost completely converted into tar.[24]

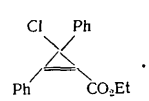
However, by carrying out the process in a flow reactor, a short residence time of the products in the hot zone and a large dilution of the reaction mixture with the initial acetylene can be achieved so that cyclopropene esters are obtained in preparative yields (30–35%).[7,24] This method in particular was used to synthesise ethyl 1-methyl- and 1,2-dimethyl-cyclopropene-3-carboxylates (yields 28–30%) from gaseous acetylenes and ethyl diazoacetate:[7,24]




In the cyclopropenation of unsaturated compounds, diazirines can be used as diazo components.[37] However, only one example of the use of the latter to obtain cyclopropene esters is known—the synthesis of ethyl 1,2-diphenyl-3-chlorocyclopropene-3-carboxylate (II) from chlorophenyldiazirine (III) and ethyl propiolate:[38]




Unfortunately, DeBoer[38] did not discuss the reasons for the formation of ester (II) instead of the expected ester (IV)



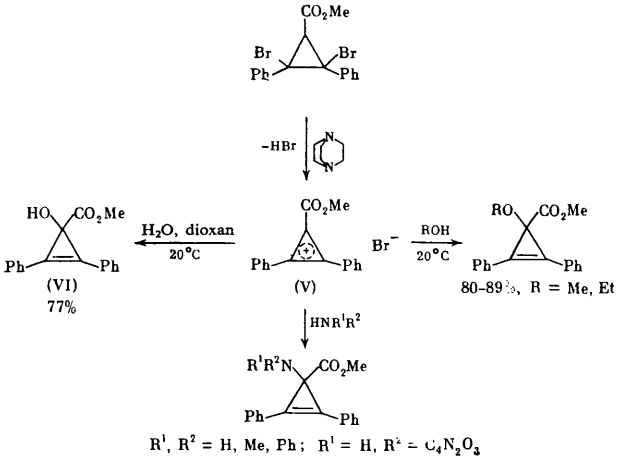

It is possible that the reaction, without involving phenylchlorocarbene, takes place as a [1,3]-dipolar addition of diazobenzyl chloride $N_2$=C(Cl)Ph, which is an isomer of (III),[37,39] to ethyl propiolate followed by elimination of nitrogen and migration of chlorine.

† Ester (I) was obtained as a solution in $CCl_4$.[26,27]

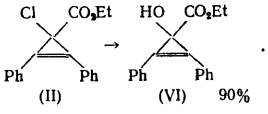
## III. Other methods for synthesising cyclopropene-3-carboxylate esters

As well as the development of the diazo method, alternative processes for the synthesis of cyclopropene-3-carboxylate esters have been elaborated. Thus, according to the findings of Komendantov et al.,[40,41] 3-hydroxy-, 3-alkoxy-, and 3-aminocyclopropene-3-carboxylate esters can be obtained from methyl 1,2-dibromo-1,2-diphenylcyclopropane-3-carboxylate by a scheme that involves formation of the cyclopropenyl bromide (V) (Scheme 1).

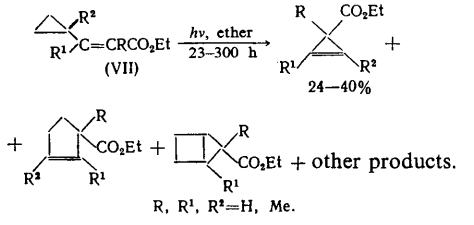
Scheme 1




In addition to this method, 1,2-diphenyl-3-hydroxycyclopropene-3-carboxylate esters (VI) can be obtained from the corresponding 3-chlorocylopropene-3-carboxylate esters (II) by treatment of a solution of (II) in acetone at 25 °C with sodium bicarbonate:[38]



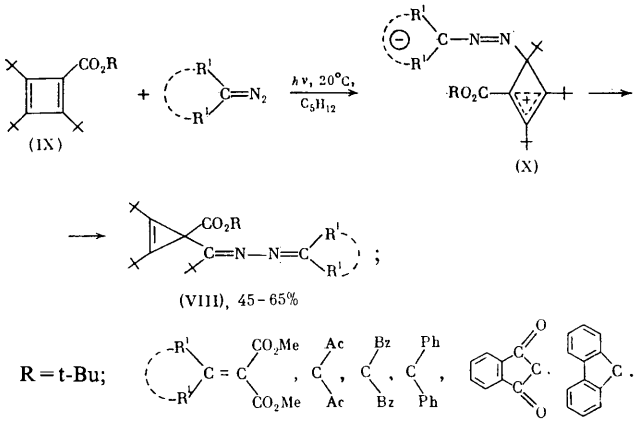

Cyclopropene esters are also obtained by the photolytic decomposition of cyclopropylvinylcarboxylate esters (VII).[42]




However, the reaction is not selective, and the yields of cyclopropenes do not exceed 40%.

Examples are known of the synthesis of tetrasubstituted cyclopropene-3-carboxylate esters (VIII) by photochemical reaction of a cyclobutadienecarboxylate ester (IX) with diazo compounds.[43]

It has been suggested that the reaction takes place via an intermediate betaine structure (X)




However, these methods are specific in nature and do not have wide importance for preparative synthesis.

## IV. Chemical reactions of cyclopropene-3-carboxylate esters

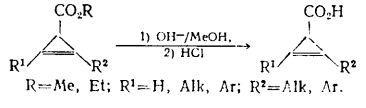
Cyclopropene-3-carboxylate esters constitute a class of alicyclic compounds with unique properties since they contain several interdependent reaction sites in the molecule—an ester group, a ring double bond and a strained three-carbon ring. In a number of cases by choosing the conditions it is possible to achieve reaction selectivity on one of the reaction sites. This fact is of importance for preparative synthesis since it is possible to obtain synthons with a three-carbon ring or carbofunctional acyclic compounds.

### 1. Reactions taking place with preservation of the three-carbon ring

#### (a) Reactions involving the ester group

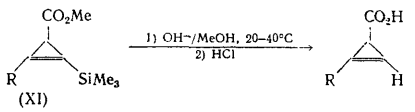
Cyclopropene-3-carboxylate esters undergo reactions that are typical for esters—alkaline and acid hydrolysis, reduction, nucleophilic addition of organometallic compounds. In the majority of cases these reactions take place with preservation of the three-carbon ring and can give other cyclopropene derivatives from accessible cyclopropene esters.[11,14,16,32,44-46]

**Hydrolysis.** Methyl and ethyl cyclopropene-3-carboxylates when treated with alcoholic or aqueous alkaline solutions at 20–40 °C are readily saponified to the corresponding acids (yields of 40% to 92%).[11,13,18,19,21,31,32,47,48]




When the temperature is lowered to 0 °C, the rate of hydrolysis decreases substantially,[26,27] and when it is increased to 90–120 °C, as well as saponification of the ester group exocyclic migration of the cyclopropene double bond occurs (when there is an alkyl substituent on the double bond), giving the corresponding alkylidenecyclopropanecarboxylic acids (see IV, 1b).

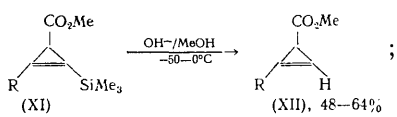
Hydrolysis of 1- or 1,2-silyl-substituted cyclopropene-3-carboxylate esters has several special features as a result of the presence of the labile C–Si bond in the molecule, and depending on the temperature and substituent in the silyl group gives different products.[26,27] Thus, at temperatures above 20 °C hydrolysis of 1-trimethylsilyl-2-alkylcyclopropene-3-carboxylate esters (XI) in methanol gives the corresponding alkylcyclopropene-3-carboxylic acids with yields of up to 95%.[26,27,32]



(XI)

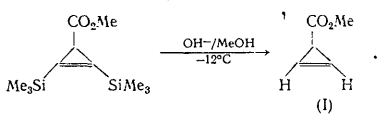
R=Alk.

On the other hand, at temperatures, of 0 °C and below only cleavage of the C–Si bond occurs in esters (XI) without saponification of the ester group. As a result, cyclopropene-3-carboxylate esters (XII) or (I) that are monosubstituted at the double bond are selectively formed:[25–29]



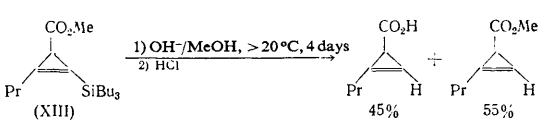
(XI) (XII), 48–64%

R=Alk.



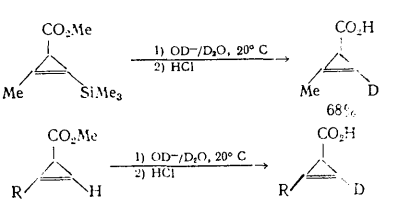
(I)

Replacement of the $SiMe_3$ group by $SiBu_3$ inhibits cleavage of the Ci–Si bond in ester (XIII) to such an extent that the reaction only takes place at temperatures above 20 °C, being accompanied by hydrolysis of the ester group and formation of a mixture of 1-propylcyclopropene-3-carboxylic acid and its methyl ester in approximately equal amounts:[26,27]



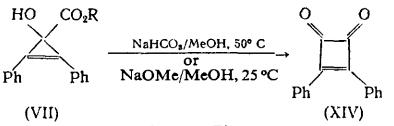
(XIII) 45% 55%

Removal of the silyl protecting group by hydrolysis in deuterated solvents gives 1-alkyl-1-deutero-substituted cyclopropene-3-carboxylic acids (the latter can also be obtained directly from the corresponding 1-alkylcyclopropene-3-carboxylate esters):[49]




R-iso-Pr, n-Bu, t-Bu.

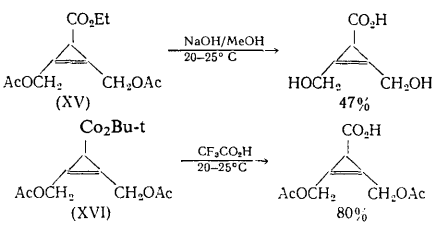
The alkaline hydrolysis of 3-hydroxycyclopropene-3-carboxylate esters (VII) takes place in an unusual manner. When these compounds are treated with bases, they undergo a reverse benzil rearrangement at the same time as hydrolysis of the ester group, as a result of which the cyclobutenedione (XIV) is formed in almost quantitative yield:[38,40]



(VII) (XIV)

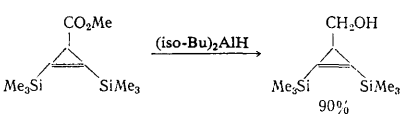
R=Me, Et.

In contrast to methyl and ethyl esters, t-butyl esters are stable to bases and only form the corresponding acids by acidic hydrolysis, which can be of use for synthetic purposes. Thus, while all the ester groups present are saponified even at room temperature when ethyl ester (V) undergoes alkaline hydrolysis, acid hydrolysis of the corresponding t-butyl ester (XVI) under mild conditions can give the corresponding acid in 80% yield.[14]

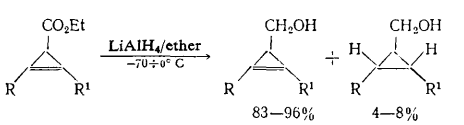


(XV) (XVI)

**Reduction to alcohols.** The ester group of cyclopropene-3-carboxylates can be reduced selectively to an alcohol with diisobutylaluminium hydride.[50]



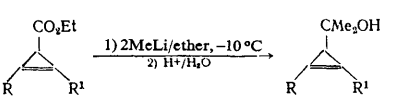

Reduction of the ester group with $LiAlH_4$ only takes place selectively at temperatures not exceeding 0 °C. In this case the cyclopropene double bond is also partially reduced.[11,51–53]




R, $R^1$=Alk, R=Me; $R^1$=$SiMe_3$.

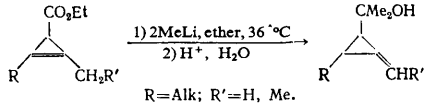
Above 0 °C only cyclopropylcarbinols are formed (see IV, 1b).

**Nucleophilic addition to the alkoxycarbonyl group.** The only examples of this type of reaction for cyclopropene-3-carboxylate esters are those that occur with methyllithium and butyllithium. Thus, at –10 °C the reaction of ethyl 1,2-dialkylcyclopropene-3-carboxylates with methyllithium in ether gives the corresponding tertiary alcohols (yields of 60–75%).[47,48]




R, $R^1$=Alk.

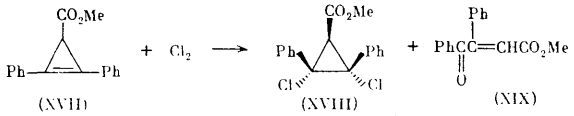
At higher temperatures, exocyclic migration of the cyclopropene double bond occurs together with alkylation, resulting in formation of the corresponding alkylidenecyclopropyldimethylcarbinols in yields of up to 70% (see IV, 1b).[47,48,54]




**(b) Reactions involving the ring double bond**

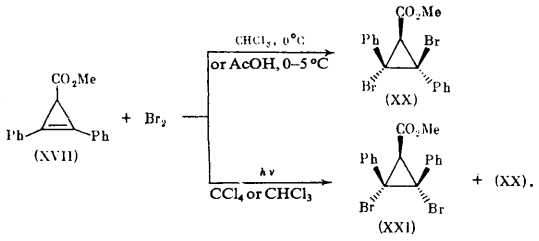
**Addition of electrophiles.** The presence of the ring double bond is responsible for the ability of cyclopropene-3-carboxylate esters to add on electrophilic reagents. In this case the ester group present has a stabilising effect on the three carbon ring,[55] and it assists in preservation of the ring and formation of the corresponding polyfunctional cyclopropanes.

Chlorination of the double bond of methyl 1,2-diphenylcyclopropene-3-carboxylate (XVII) occurs by a *cis*-addition in a *trans*-orientation relative to the ester group, and the yield of methyl dichlorocyclopropanecarboxylate (XVIII) varies from 35% to 71% depending on the reaction conditions.[56] The process is accompanied to a slight extent by opening of the cyclopropene residue and formation of the butenoate (XIX).




71% (*h*ν, $CCl_4$)
41% (diffuse light, 0 °C, $CCl_4$)
35% (AcOH, 15°C)

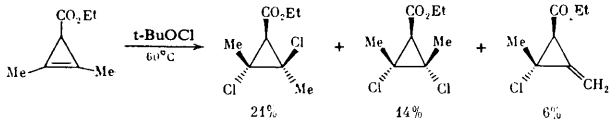
The stereochemistry of the addition of bromine to the ring double bond depends on the experimental conditions, *cis*- or *trans*-addition occurring with a *trans*-orientation relative to the ester group. Thus, bromination of ester (XVII) in chloroform or acetic acid in the dark or diffuse light takes place exclusively by *trans*-addition, giving methyl 1,2-dibromo-*cis*,*trans*-1,2-diphenylcyclopropane-3-carboxylate (XX) in 40% yield.[40]



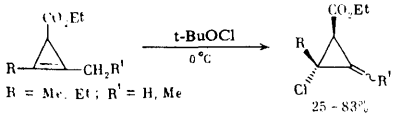

On the other hand, in tetrachloromethane or chloroform on irradiation *cis*-addition of bromine mainly takes place with formation of methyl 1,2-dibromo-*cis*,*cis*-1,2-diphenylcyclopropane-3-carboxylate (XXI) in 80% yield. In this case the isomeric ester (XX) is formed in very small quantities.[40]

It was assumed[40] that the dependence of the yields of halogenation products on the reaction conditions is due to different mechanisms for addition of chlorine or bromine to ester (XVII). An ionic mechanism is assumed in diffuse light and in a polar solvent and a radical mechanism in the presence of radiation. The higher yields of dichloro- and dibromo- cyclopropanes (XVIII) and (XXI) obtained by irradiation may be due to the higher stability of an intermediate cyclopropyl radical compared to the stability of a cyclopropyl cation or the corresponding chloronium or bromonium cations.[40,56]

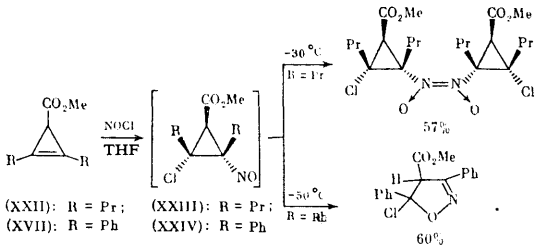
Halogenation of cyclopropene esters may also be carried out using t-butyl hypochlorite. However, in this case at 60 °C addition of chlorine is not selective and gives a mixture of *cis*- and *trans*-isomers of dichlorocyclopropanes together with methylenechlorocyclopropanes—substitution and isomerisation products.[57,58]



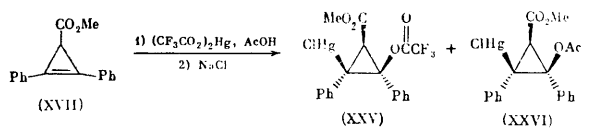

By reducing the temperature to 0 °C the reaction can be mainly directed towards formation of methylenechlorocyclopropanes; in a number of cases this can be important for preparative synthesis.[57,58]




Cyclopropene esters (XXII) and (XVII) can add on nitrosyl chloride. However, the nitrosyl chlorides (XXIII) and (XXIV) formed in this process have low stability and depending on their structure either dimerise or undergo opening of the three-carbon ring:[59]

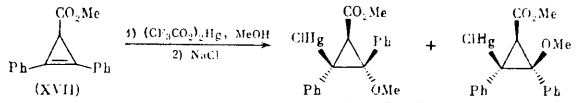



Mercuration of cyclopropene-3-carboxylate esters takes place with preservation of the cyclopropane residue,[60,61] and the reaction conditions have a considerable effect on both the stereochemistry of addition of mercury salts to the ring double bond and the nature of the resulting products formed. Thus, addition of mercuric trifluoroacetate to the diphenylcyclopropene ester (XVII) in acetic acid occurs by a *cis*-mechanism in a *cis*-orientation relative to the ester group and gives (as a result of subsequent treatment with NaCl) the 1-chloromercuro-2-trifluoroacetoxycyclopropanecarboxylate ester (XXV) together with a small quantity of the solvolysis adduct (XXVI); the ratio of (XXV) : (XXVI) = 87 : 13.[61]

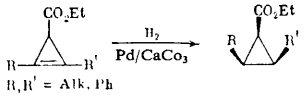



Reaction of the same ester (XVII) with mercuric trifluoroacetate in methanol leads exclusively to solvolysis adducts—the corresponding 1-chloromercuro-2-methoxycyclopropanes (XXVII)— with the

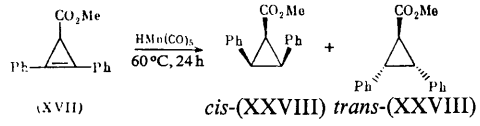
*trans,cis*-isomer, which is formed by *trans*-addition, predominating [ratio of *trans,cis*-(XXVII) : *cis,cis*-(XXVII) = 85 : 15).[60,61]



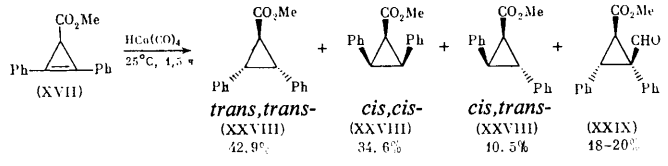

**Reduction.** The ring double bond of cyclopropenecarboxylate esters is reduced by metal carbonyl hydrides, lithium aluminium hydride, and hydrogen in the presence of catalysts. The most selective and frequently used method is reduction of cyclopropene esters by catalytic hydrogenation using palladium supported on $CaCO_3$ as the catalyst. As a result, only *cis,cis*-1,2-dialkylcyclopropane-3-carboxylate esters are formed in yields up to 98%.[18,19,42,62,63]




Reduction of methyl diphenylcyclopropenecarboxylate (XVII) with manganese pentacarbonyl hydride is not stereospecific and gives a mixture of isomeric cyclopropanecarboxylate esters in quantitative yield, although the *cis*-isomer is mainly formed [ratio of *cis*-(XXVIII) : *trans*-(XXVIII) = 7 : 1]: [64]

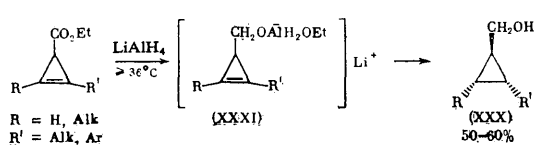



Reduction of the same ester (XVII) with cobalt carbonyl hydride is not selective and all possible isomeric 1,2-diphenylcyclopropane-3-carboxylate esters (XXVIII) are formed with a total yield of 88%.[65]



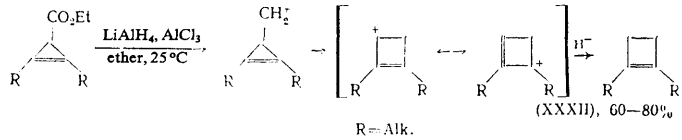

In this case hydroformylation of ester (XVII) is a competing process, resulting in the formation of ester (XXIX) with a yield of about 22%.

In contrast to the reagents considered above, lithium aluminium hydride mainly reduces the ester group in cyclopropene esters, and depending on the temperature reduction can also be accompanied by hydrogenation of the ring double bond. Thus, at 0 °C only cyclopropene alcohols are formed (see IV, 1a), while at higher temperatures the corresponding cyclopropylcarbinols are formed, only as a single *trans,trans*-isomer (XXX).[51–53]



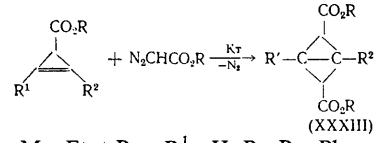

The stereospecific formation of (XXX) is due, according to Vincens et al.,[51,53] to the intramolecular nature of the reduction of the double bond in the intermediate alkoxyaluminium hydride (XXXI).

In the presence of $AlCl_3$ reduction of cyclopropene esters with $LiAlH_4$, which occurs via intermediate carbocations, is accompanied by expansion of the three-membered ring and formation of cyclobutenes (XXXII).[66]




**Cycloaddition.** Because of the presence of the double bond, cyclopropene-3-carboxylate esters undergo a cycloaddition reaction with various enophiles to give the corresponding bicyclo[*n*.1.0]-carboxylate esters ($n$ = 1–4). In a number of cases these reactions are important for preparative synthesis.

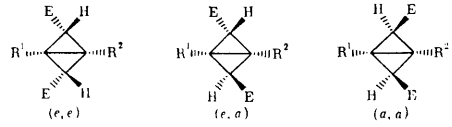
**[1 + 2]-Cycloaddition.** The only known example of reactions of this type is the addition of alkoxycarbonylcarbenes, which are generated by catalytic decomposition of alkyl diazoacetates, to the double bond of cyclopropene esters. In this process the corresponding bicyclobutane adducts (XXXIII) are formed in 25–42% yield:[67–70]




R = Me, Et, t-Bu; $R^1$ = H, Pr, Bu, Ph; $R^2$ = Pr, Bu, Ph, $SiMe_3$; Cat = Cu (110 °C), $Rh(OAc)_2$ (25 °C).

In certain cases diesters (XXXIII) are formed as by-products (2–5%) in the preparation of cyclopropene esters from acetylenes and alkyl diazoacetates.[14,28,71]

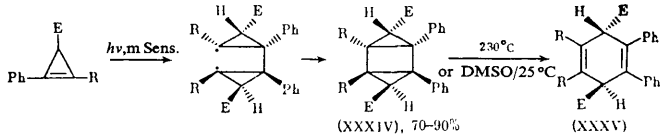
As regards the stereoselectivity of this reaction, it is known that di-t-butyl esters (XXXIII) are only formed as a single (*e,e*)-isomer,[14] while the dimethyl and diethyl esters are formed as two (*e,e*)- and (*e,a*)-isomers, the ratio of which varies from 3 : 1 to 1 : 1 depending on the nature of the substituents $R^1$ and $R^2$.[28,67–70,71] The sterically hindered (*a,a*)-isomer is not formed in a single case.




E = $CO_2Me$, $CO_2Et$, $CO_2Bu$-t

**[2 + 2]-Cycloaddition.** Reactions of this type involving cyclopropene-3-carboxylate esters only occur on photolysis and have limited importance for preparative synthesis. In particular, homodimerisation of cyclopropene esters to the corresponding tricyclohexanedicarboxylate esters (XXXIV) in the presence of a sensitiser (for example, trioxanone) takes place stereospecifically via biradical intermediates which are characterised by the greatest delocalisation of electrons.[72–76] Esters (XXXIV) when heated to

230 °C or when dissolved in dimethyl sulphoxide at 25 °C are quantitatively converted to cyclohexadienedicarboxylate esters (XXXV).[72]

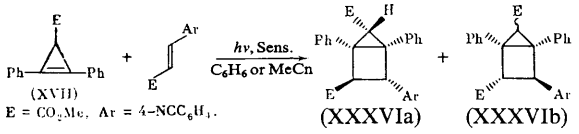



R = Me, Ph; E = $CO_2Me$.

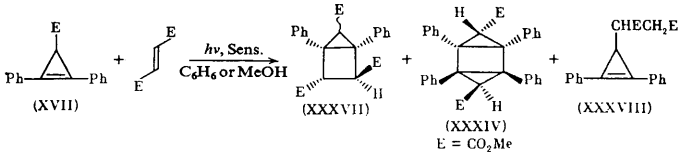
In two studies[77,78] there are reports about the possible formation of tricyclohexanes (XXXIV) together with the isomeric cyclohexadienes (XXV) [77] by carrying out this reaction with direct photolysis. However, attempts to reproduce the reported results[77,78] proved unsuccessful;[72–76] cyclopropene esters underwent opening of the three-carbon ring with formation of alkoxyfurans. This difference in the behaviour of cyclopropene esters under conditions of direct and sensitised photolysis is attributed[72–76] to the different multiplicity of the excited state of cyclopropene.

According to the results of two studies[72,79] photochemical cyclodimerisation of 3-substituted cyclopropene-3-carboxylate esters doe not occur because of considerable steric hindrance.

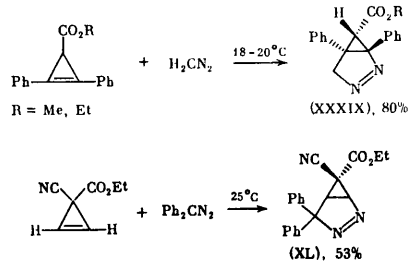
There are known examples of the cross-[2 + 2]-cycloaddition of cyclopropene esters to electron-deficient olefins taking place by sensitised photolysis.[74] Thus, the photochemical reaction of ester (XVII) with methyl *p*-cyanocinnamate gives the corresponding bicyclopentane adducts (XXXVIa, b) with an *exo*-configuration of the alkoxycarbonyl group.



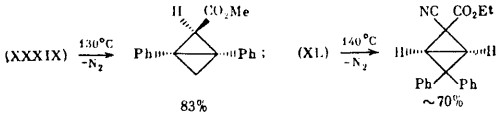

However, the reaction of the same ester (XVII) with dimethyl fumarate is less sensitive, and both the bicyclopentane *exo*- and *endo*-isomers (XXXVII) are formed.



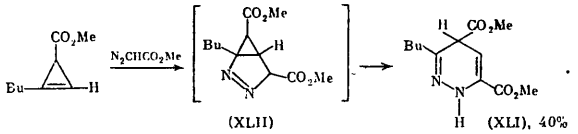

**[3 + 2]-Cycloaddition.** In the absence of decomposition catalysts diazoalkanes react at room temperature with cyclopropene-3-carboxylate esters by a [3 + 2]-cycloaddition to give the corresponding pyrazolines solely as their *exo*-isomers.[80–82]




The reaction can have preparative value for the synthesis of bicyclo[1.1.0]butanecarboxylate esters, which are formed in high yield by thermolysis of pyrazolines (XXXIX) or (XL).[80,82]

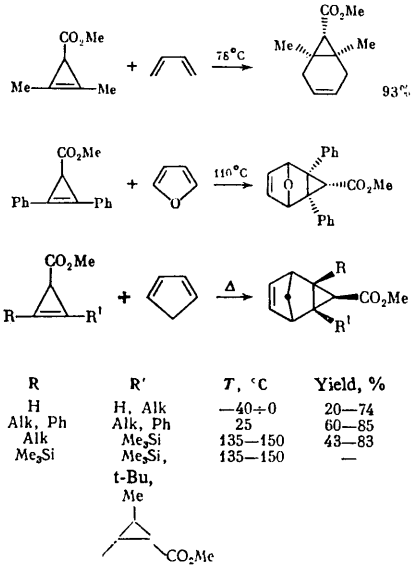



The reaction of methyl 1-butylcyclopropene-3-carboxylate with methyl diazoacetate in the absence of catalysts also apparently takes place by a [3 + 2]-cycloaddition [via the initially formed bicyclic pyrazoline (XLII)] to give the pyridazine (XLI):[70]




**[4 + 2]-Cycloaddition.** These are the most characteristic of all the cycloaddition reactions of cyclopropene-3-carboxylate esters and are those the most frequently used in synthesis.

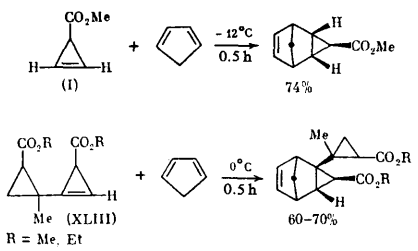
Cyclopropene esters react with butadienes,[83,84] cyclopentadiene,[27–29,30,84–87] and furan[85,87] to form the corresponding adducts, the reactions with cyclic dienes taking place with strict selectivity. When cyclopropene esters are reacted with cyclopentadiene, the *endo*-adducts are exclusively formed, and with furan the corresponding *exo*-adducts are formed.




| R | R' | *T*, °C | Yield, % |
|---|---|---|---|
| H | H, Alk | −40÷0 | 20—74 |
| Alk, Ph | Alk, Ph | 25 | 60—85 |
| Alk | $Me_3Si$ | 135—150 | 43—83 |
| $Me_3Si$ | $Me_3Si$, t-Bu, Me | 135—150 | — |

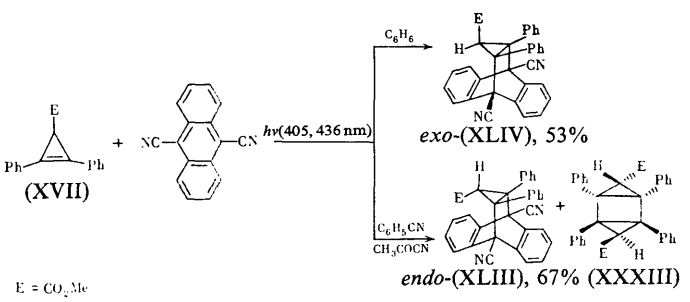
The activity of cyclopropene esters as dienophiles is determined by the nature of the substituents on the ring double bond and the steric accessibility of this bond. Thus, unsubstituted and monosubstituted cyclopropene-3-carboxylate esters are the most active, reacting with cyclopentadiene even at 0 °C and below.[27,29,86] Because of this it was possible to use cyclopentadiene as a trap for cyclopropene esters that have low stability under normal conditions. It was this method that

was used to "capture" the simplest methyl cyclopropene-3-carboxylate (I) and esters (XLIII), which are unstable in a pure state above 0 °C.[27,29,86]



The least active dienophiles are cyclopropene esters with a trimethylsilyl group on the double bond, which form the corresponding adducts only on boiling in xylene for many hours; and the introduction of a further trimethylsilyl or other bulky substituent on to the ring double bond completely prevents a reactions with cyclopentadiene.[27,28,86]

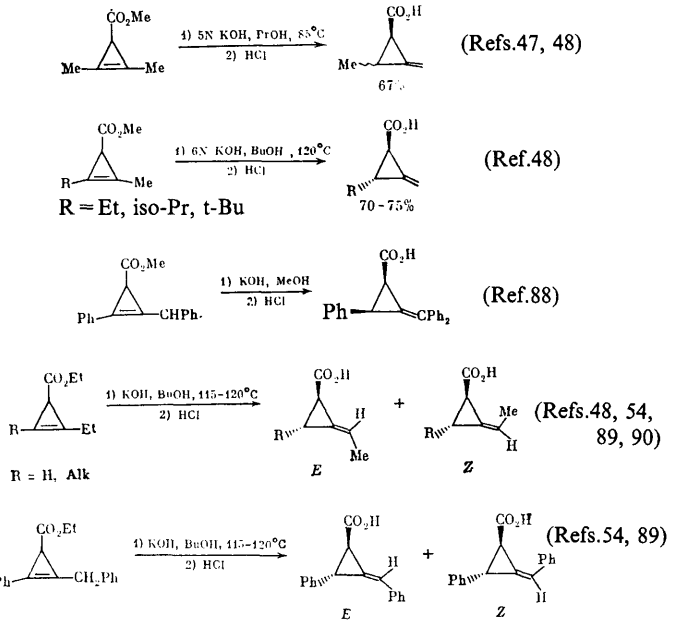
[4 + 2]-Cycloaddition reactions of cyclopropene esters with electron-deficient dienes are also possible by photolysis, with the structure of the adducts formed depending to a considerable degree on the experimental conditions. Photochemical reaction of ester (XVII) with 9,10-dicyanoanthracene in benzene gives the *exo*-adduct (XLIV), while in acetonitrile or benzonitrile the sterically hindered *endo*-adduct (XLIII) is formed. In the latter case the cyclodimer (XXXIII) is also formed together with *endo*-adduct (XLIII).



This difference in the results of the reaction was attributed by Brown-Wensley et al.[74] to differences in the nature of the intermediates in relation to the polarity of the medium.

**Exocyclic migration of the double bond.** In a number of unsaturated compounds with a three-carbon ring, compounds with an *exo*-configuration of the double bond are thermodynamically more stable than the isomeric alkylcyclopropenes; this causes the latter to be isomerised to the corresponding alkylidenecyclopropanes by the action of bases.[55]

Exocyclic migration of the double bond in alkyl- or benzyl-substituted cyclopropene-3-carboxylate esters occurs, in addition to saponification of the ester group, on treatment with alcoholic alkali solutions at 85–120 °C.[47,48,54,88–90] As a result, 1-methylenecyclopropane-3-carboxylate esters are formed from 1-methylcyclopropene-3-carboxylate esters, while 1-ethyl- or 1-benzyl-substituted cyclopropene-3-carboxylate esters give 1-ethylidene- or 1-benzylidene-cyclopropane-3-carboxylate esters as mixtures of their (*Z*)- and (*E*)-isomers with the latter predominating.



Potassium t-butoxide and sodium methoxide in absolute solvents do not cause cyclopropene esters to react in these ways.[91]

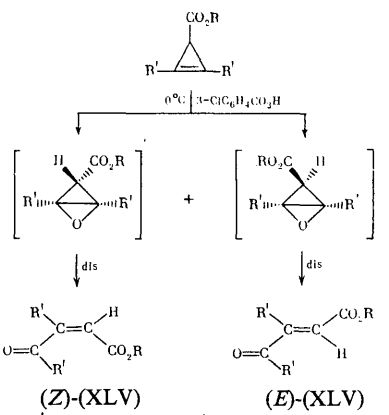
## 2. Reactions of cyclopropene-3-carboxylate esters with opening of the three-carbon ring

The reactions discussed in the previous section indicate that the three-carbon ring of cyclopropene-3-carboxylate esters, in particular for those disubstituted on the double bond, is quite stable. However, acids, oxidising agents or transition metals can cause the ring to open with formation of acyclic compounds.

### (a) Oxidation

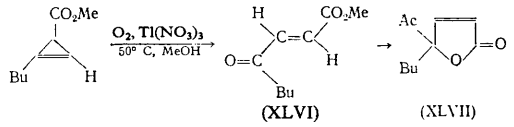
Oxidation of cyclopropene-3-carboxylate esters with chloroperbenzoic acid at 0 °C takes place via an epoxidation stage and gives isomeric unsaturated ketones (XLV) in almost quantitative yields (Scheme 2).[92–95]

Scheme 2

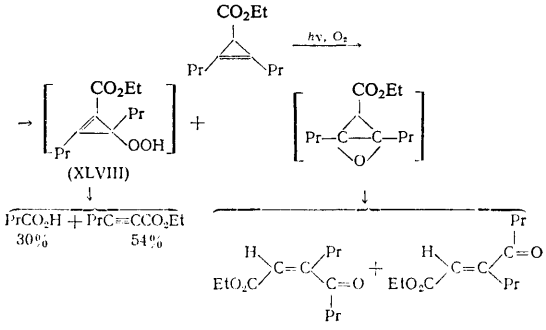


Peracetic and perbenzoic acids do not cause cyclopropene esters to react at all.[94]

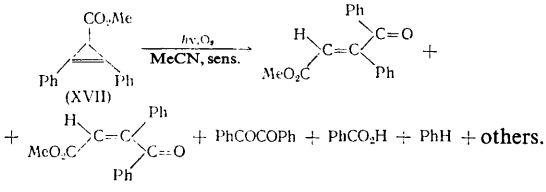
The formation of vinylketone (XLVI) occurs in the oxidation of methyl 1-butylcyclopropene-3-carboxylate with oxygen in the presence of thallium nitrate at 50 °C in methanol. However, (XLVI) is gradually converted during the reaction to lactone (XLVII).[70]




In the oxidation of cyclopropene esters with oxygen by sensitised photolysis, the yield of vinylketones does not exceed 15%. The main products of the photooxidation of 1,2-dipropylcyclopropene-3-carboxylate esters are butyric acid and ethyl hex-2-ynoate, which are formed as a result of decomposition of the initially generated hydroperoxide (XLVIII).[95]



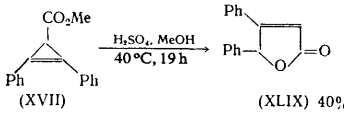

The photooxidation of ester (XVII) is not selective and leads to a complex mixture of products.[74]



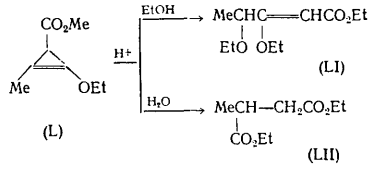

**(b) Reactions with acids**

Cyclopropene-3-carboxylate esters are fairly stable towards acids. At 20–25 °C they withstand prolonged contact (up to 40 h) with concentrated hydrochloric, hydrobromic, sulphuric, and hydrofluoric acids.[96,97] However, on boiling with alcoholic or aqueous acid solutions cyclopropene esters undergo ring-opening to form various carbofunctional compounds.

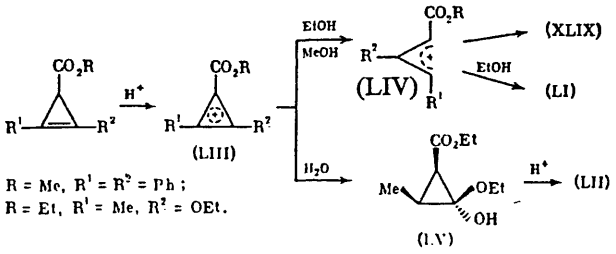
Thus, when ester (XVII) is boiled for many hours with a methanol solution of sulphuric acid, lactone (XLIX) is obtained.[96]




Under similar conditions the ethoxycyclopropene-3-carboxylate ester (L) is converted to ethyl diethoxypentenoate (LI) in 50% yield, while in an aqueous solution of *p*-toluenesulphonic acid the diethyl ester (LII) is obtained in quantitative yield without formation of the corresponding furanone.[98]

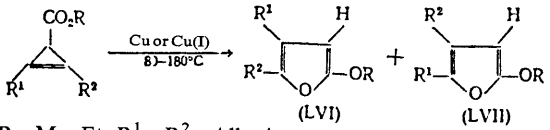



It has been proposed[96,98] that the driving force of all these processes is protonation of the ring double bond to form the cyclopropyl cation (LIII), which isomerises in alcohol solution to the allylic cation (LIV), which then cyclises to lactone (XLIX) or reacts with the solvent to form acid (LI). In aqueous solution hydration of cation (LIII) gives ketal (LV), which is isomerised by the action of acid to ester (LII).




**(c) Catalytic reactions of cyclopropene-3-carboxylate esters**

**Reactions of cyclopropene-3-carboxylate esters on treatment with copper compounds.** The most numerous examples of catalytic reactions of cyclopropene esters are those occurring in the presence of copper compounds. Among these the isomerisation of cyclopropene-3-carboxylate esters to alkoxyfurans is the most familiar.[21,55,99,100]

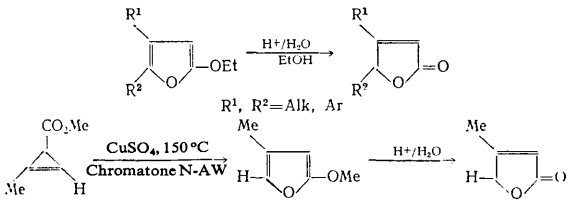



R = Me, Et, $R^1 = R^2$ = Alk, Ar;
R = Et, $R^1$ = Me, $R^2$ = Ph (LVI : LVII = 19 : 1), n-Bu (LVI : LVII = 1 : 1) t-Bu (LVI : LVII = 1.2 : 1);
R = Et, $R^1$ = Et, t-Bu, $R^2$ = H.

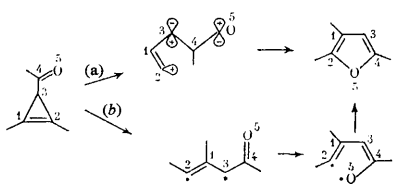
In an inert atmosphere with exclusion of moisture alkoxyfurans are the main reaction products, so this can be regarded as a preparative method.[55,99,100]

Asymmetrically substituted cyclopropene-3-carboxylate esters are converted to form two isomeric alkoxyfurans (LVI) and (LVII) in total yields of up to 90%, the ratio of which is determined by the substituents on the cyclopropene double bond.[100] Isomerisation of 1-substituted cyclopropene-3-carboxylate esters only gives product (LVI), which corresponds to cleavage of the C(2)–C(3) bond of the cyclopropene ring.[7,22] However, the yield of alkoxyfuran (LVI) does not exceed 20–25%, which is apparently due to oligomerisation of the initial cyclopropene ester and final alkoxyfuran during the reaction.

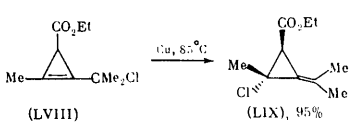
In the presence of traces of moisture and acids, alkoxyfurans are readily hydrolysed to the corresponding furanones,[19,100] which in specific cases[7] are the only identifiable reaction products.



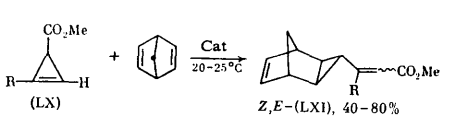

According to Komendantov et al.,[100] the formation of alkoxyfurans can take place either by a concerted [1,3]-sigmatropic rearrangement of cyclopropene esters [route (*a*)], which is no longer forbidden in the presence of a catalyst, or by a non-concerted route (*b*) via a biradical that is formed by opening of the three-membered ring. In this case the role of the catalyst is to reduce the energy of activation for isomerisation through the formation of an organocopper complex and hence weaken the σ-bonds.



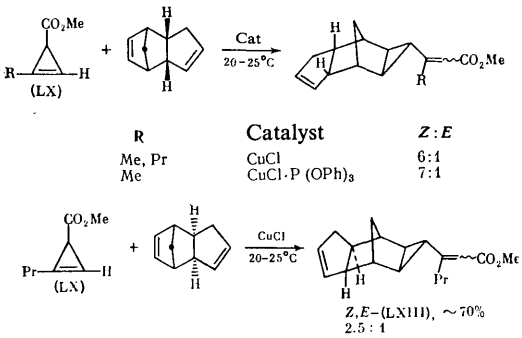

However, for cyclopropene ester (LVIII), which contains a chlorine atom in the α-position of the alkyl substituent on the double bond (in contrast to the esters considered above), in the presence of copper at 85 °C an exocyclic migration of the double bond and chlorine to form the ester (LIX) occurs rather than isomerisation to an alkoxyfuran.[101] The same reaction of ester (LVIII) occurs without copper but at a higher temperature (150 °C).




Comparatively recently[102,103] it was found that 1-alkylcyclopropene-3-carboxylate esters (LX) in the presence of Cu(I) compounds can selectively vinylcyclopropanate the strained ring double bond in norbornadiene and dicyclopentadiene to give cycloadducts (LXI)–(LXIII) exclusively as the *exo,anti*-isomers. In this case the ratio of (*Z*)- to (*E*)-isomers varies according to the nature of the substituent R in the cyclopropene ester, the structure of the unsaturated compound and the nature of the catalyst, increasing substantially on changing from CuCl to its complexes.[103]

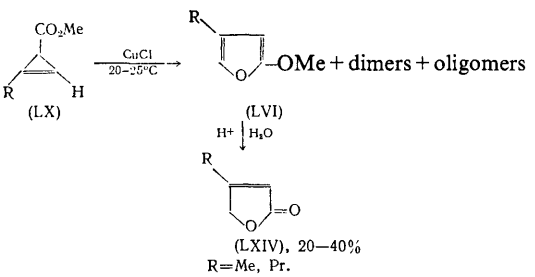



| R | Catalyst (Cat) | *Z*:*E* |
|---|---|---|
| Me | CuCl | 1.3:1 |
| | CuCl·2Me$_3$SiC≡CMe | 2.5:1 |
| | CuCl·P (OPh)$_3$ | 3:1 |
| Pr | CuCl | 1.7:1 |
| | CuCl·2Me$_3$SiC≡CMe | 2.5:1 |
| | CuCl·P (OPh)$_3$ | 4:1 |
| $C_5H_{11}$ | CuCl | 1.8:1 |
| | CuCl·P (OPh)$_3$ | 7:1 |



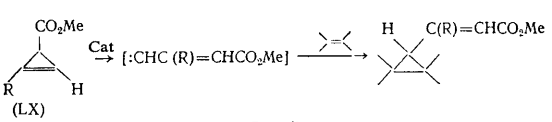

| R | Catalyst | *Z*:*E* |
|---|---|---|
| Me, Pr | CuCl | 6:1 |
| Me | CuCl·P (OPh)$_3$ | 7:1 |

With other unsaturated compounds—1,5-cyclooctadiene, cyclohexene, methylenecyclobutane, methyl acrylate—esters (LX) do not give vinylcyclopropane adducts but are converted to lactones (LXIV), as a result of hydrolysis of the initially formed alkoxyfurans (see above), and oligomers.[103]



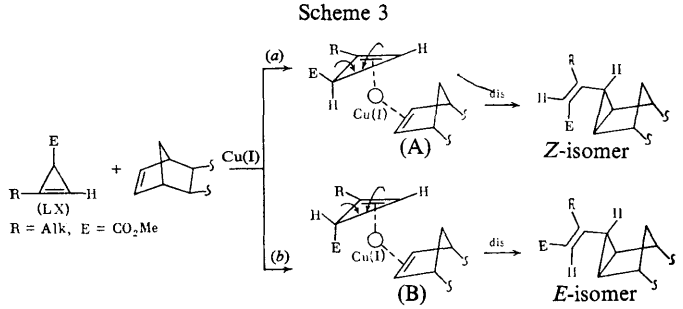

When esters (LX) are reacted with cyclopentadiene, diene adducts are formed in 70% yield.[103]

According to the results of three studies[102,104,105] the formation of cycloadducts (LXI)–(LXIV) may be due to addition to the double bonds of vinylcarbene intermediates which are generated by catalytic isomerisation of cyclopropenes (LX).




However, the high regioselectivity and stereoselectivity for formation of the vinylcyclopropane adducts is more consistent with the reaction taking place within the coordination sphere of Cu(I) according to a concerted mechanism (Scheme 3).[103]

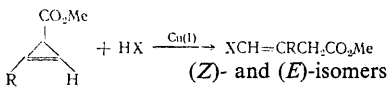
Scheme 3




In this case the exclusive *exo*-addition of the reaction species to the double bond of norbornadiene is due to *exo*-coordination of the copper atom with the initial cyclodiene. The selective formation of

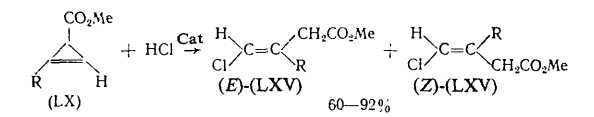
the *anti*-isomer and the ratio of (*Z*)- to (*E*)-isomers are established when cyclopropene (LX) coordinates with the olefin complex of univalent copper and is determined by the stereoselectivity of the subsequent conversions, being governed by the principle of conservation of orbital symmetry. The presence of bulky ligands in the coordination sphere of copper, particularly when changing from CuCl to the complex catalysts $2MeC{\equiv}CSiMe_3.CuCl$ and $(PhO)_3P.CuCl$, must reduce the probability of coordination of the type (B) in favour of (A), in other words, it leads to an increase in the yield of (*Z*)-isomer, which in actual fact occurs.

During the last few years we have discovered a new reaction of methyl 1-alkylcyclopropene-3-carboxylates (LX) with proton-donor reagents of the general type HX, which takes place on treatment with copper(I) chloride at room temperature. This reaction, which is undoubtedly of interest for preparative synthesis, leads to the formation of the corresponding (*Z*)- and (*E*)-isomers of 4-substituted methyl 3-alkylbutenoates.[97,106-108]

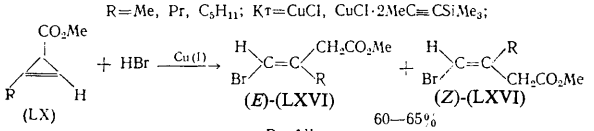


R=Alk, X=Cl, Br, $R^1CO_2$, ArO, CN, $R^2C{\equiv}C$.

Gaseous HBr, hydrochloric acid, and hydrogen chloride (whatever the method of generation) at 20–25 °C in the presence of copper (I) chloride or its complex readily add on to the C(2)–C(3) bond in (LX) to form methyl 4-bromo- or 4-chloro-butenoates (LXV) and (LXVI), mainly as their (*E*)-isomers.[97,106]

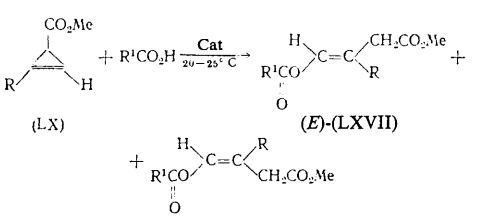


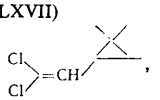
R=Me, Pr, $C_5H_{11}$; Kт=CuCl, $CuCl{\cdot}2MeC{\equiv}CSiMe_3$;



R=Alk.

Carboxylic acids whose $pK_a$ values occur within the region 3 to 7 (monochloroacetic, formic, acrylic, acetic, permethrinic) react in a similar manner with cyclopropene esters (LX). In this case the yields of the resulting (*Z*)- and (*E*)-4-acyloxybutenoate esters (LXVII) amount to 58–95%.[97,106]

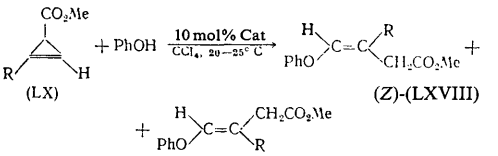


R=Alk, $R^1$=H, $CH_2Cl$, $H_2C{=}CH$, Me, ,

$Cat = CuCl.2MeC{\equiv}CSiMe_3$

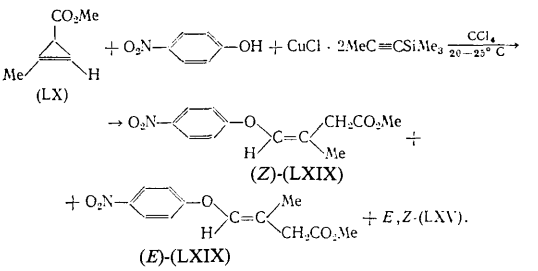
Stronger carboxylic acids that have $pK_a$ values of 0–2 (trifluoro-, trichloro-, and dichloro-acetic acids as well as hydrofluoric acid) do not add on to cyclopropene esters (LX) in the presence of CuCl but rapidly convert them to 4-alkylfuranones (LXIV).[97]

On the other hand the catalytic addition of phenol to esters (LX) proceeds quite smoothly, giving methyl phenoxybutenoates (LXVIII) in 50–80% yield, mainly as the (*Z*)-isomer.[97,106]



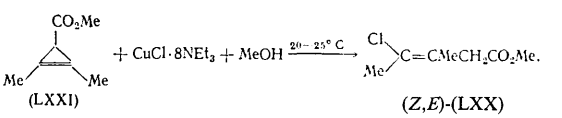
R = Me, $C_5H_{11}$; Cat = $CuCl.2MeC{\equiv}CSiMe_3$.

Reaction of esters (LX) with 4-nitrophenol under the same conditions gives mainly oligomeric products. However, in the presence of 100 mol% of an acetylene complex of copper(I) chloride, *p*-nitrophenol an add on to a cyclopropene ester (LX, R = Me) in a similar manner to phenol to form (*Z*)- and (*E*)-methyl 4-(*p*-nitrophenoxy)-3-methylbut-3-enoates (LXIX) (5 : 1) with a total yield of 30%. The main reaction products here are isomeric 4-chloro-3-methylbut-3-enoate esters (LXV) (total yield 45%),[97] in the formation of which nitrophenol appears only as a proton donor, while CuCl is a source of Cl, in other words, it acts as a reactant rather than a catalyst:



This trend is shown to an even greater extent for 2,4-dinitrophenol, methanol, butyl mercaptan, and 5-methyl-4-cyclohexene-1,2-dicarboximide. Their reaction with esters (LX) in the presence of the complex $CuCl.2MeC{\equiv}CSiMe_3$ gives only (*Z*)- and (*E*)-4-chlorobutenoate esters (LXV), the quantity of which increases as the amount of added CuCl increases.[97]

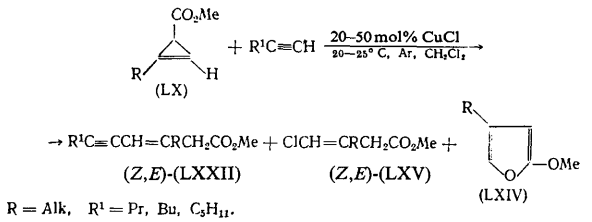
The only example of the catalytic addition of HCl units to 1,2-disubstituted cyclopropene-3-carboxylate esters is formation of the corresponding 4-chloropentenoate esters (LXX) by reaction of the cyclopropenoate ester (LXXI) with an equivalent quantity of the complex $CuCl.8NEt_3$ and methanol.[106]



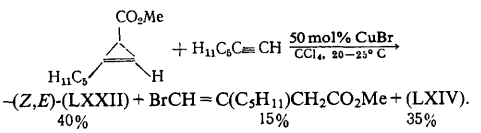
Esters (LXX) are formed in 30% yield mainly as the (*Z*)-isomer [(*Z*) : (*E*) = 5 : 2].

Among compounds that contain a mobile hydrogen atom on a carbon atom (terminal acetylenes, HCN, nitro- and trinitro-methane, ethyl cyanoacetate, bromoform) an [H–X]-addition reaction with 1-alkylcyclopropene-3-carboxylate esters can only be achieved with

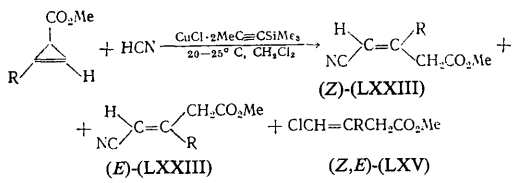
terminal acetylenes and HCN,[97,107] which, in contrast to the other compounds with a mobile hydrogen atom that were studied, are able to form complexes with CuCl. In this case esters (LX) and 1-alkynes in the presence of 20–50 mol% CuCl react to form the corresponding 3-alken-5-ynoate esters (LXXII) (yield ~65%) mainly as their (*Z*)-isomers[105] together with chlorobutenoate esters (LXV) (yields 10–20%) and methoxyfurans (LXIV) (yield 5–10%). The selectivity of the process and the yields of esters (LXXII) depend significantly on the reaction conditions, primarily on the ratio of reactants and the relative quantity of CuCl.[97,107]




The reaction of cyclopropene ester (LX, R = $C_5H_{11}$) with 1-heptyne in the presence of CuBr occurs in a similar manner:[97]



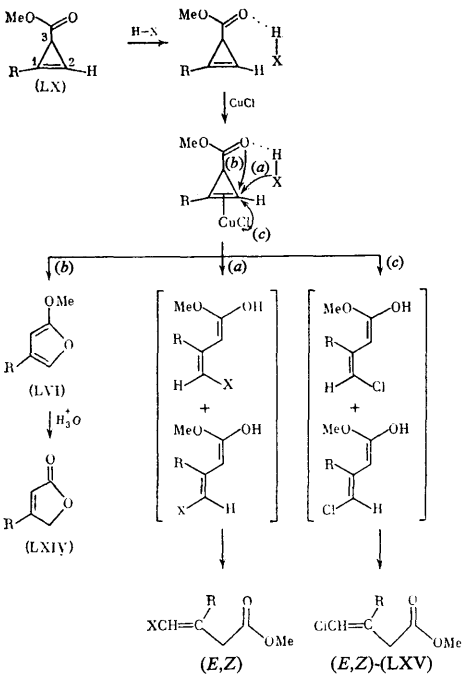

Addition of gaseous HCN in the presence of CuCl.2MeC≡CSiMe$_3$ to cyclopropenes (LX) also takes place fairly readily, the formation of 4-cyanoalkylbutenoate esters (LXXIII) also being accompanied by partial hydrochlorination of (LX) to chlorobutenoate esters (LXV). The maximum yield of esters (LXXIII) (60–65%) occurs with incomplete conversion of (LX) (66–70%) and a quantity of CuCl.2MeC≡CSiMe$_3$ equal to 20 mol%.[107]




Treatment of esters (LX) with trinitromethane, nitromethane, bromoform, or ethyl acetate at 25 °C in the presence of 10–100 mol% of $CuCl_2$.2MeC≡CSiMe$_3$ complex gives only chlorobutenoate esters (LXV).[97]

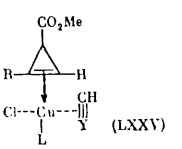
As regards the mechanism of the reaction between cyclopropene esters and proton-donor reagents HX (Scheme 4), it is most likely that the formation of 4-substituted 3-butenoate esters takes place within the coordination sphere of copper.[97] In the presence of the reagents HX (hydrogen halides, carboxylic acids, phenols) that are capable of solvating cyclopropene esters (LX) and thus become part of an organocopper complex, attack by nucleophile X on the C(2) atom of the ring becomes possible and (*Z*)- and (*E*)-methyl 4-X-3-alkyl-3-butenoates are formed [route (*a*)].

Scheme 4




This process is significant or fundamental (yield of products 30–95%) in the case of HCl, HBr, carboxylic acids with p$K_a$ 3–7, phenol, and nitrophenol. In the presence of carboxylic acids with p$K_a$ 0–2, isomerisation to a methoxyfuran is preferred [route (*b*)], apparently because of the low nucleophilicity of residue X.

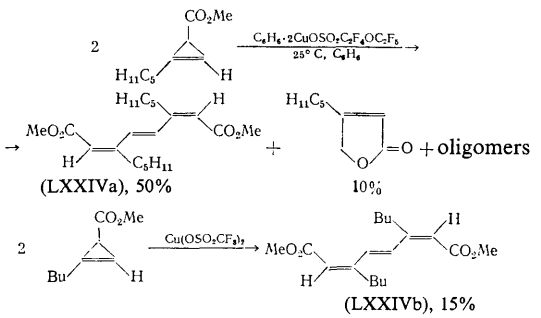
The formation of addition product by catalytic reaction of cyclopropene esters with terminal acetylenes and HCN takes place according to the same scheme. However, in this case the reagents HX are drawn into the reaction zone by formation of a complex with CuCl:




In the resulting organocopper intermediate (LXXV) coordination of the terminal acetylenes or HCN with CuCl leads to weakening of the C–H bond, an increase in the nucleophilicity of the C≡Y residue and convergence of the proton-donor reagent with the cyclopropene molecule, thus creating a favourable opportunity for nucleophilic attack on the C(2) atom to form the corresponding enynoate or cyanobutenoate esters (LXXII) and (LXXIII).[97]

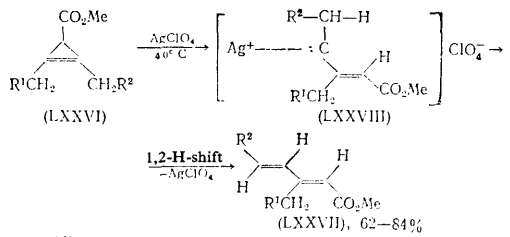
In the reaction of cyclopropene esters with HX reagents in the presence of CuCl, a competing process is also possible—addition of HCl units to the C(2)–C(3) bond to form (*Z*)- and (*E*)-methyl 4-chloro-3-alkyl-3-butenoates (LXV) [route (*c*)]. In this case the HX reagents only act as proton donors, while CuCl acts as the chlorine donor. This route is the main one for reactions of the esters in the presence of 20–100 mol% CuCl with methanol, 2,4-dinitrophenol, butyl mercaptan, cyclohexenedicarboximide, bromoform, trinitromethane, nitromethane, and ethyl cyanoacetate.

When CuCl or its complexes are replaced by $CuOSO_2C_2F_4OC_2F_5$ or copper(II) triflate, the main reaction route of 1-alkylcyclopropene-3-carboxylate esters is their stereoselective dimerisation with ring-opening to give hexatrienecarboxylate esters (LXXIV), which are the formal dimers of vinylcarbenes [:CHC(R)=CHCO$_2$Me] isomer with (LX).[70,109]



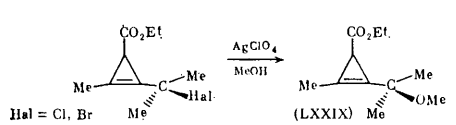

The same reaction of (LX) on treatment with $CuOSO_2C_2F_4OC_2F_5$ occurs in the presence of norbornadiene or acetic acid; neither vinylcyclopropene adducts (LXI) nor acyloxybutenoate esters (LXVII) ($R^1$ = Me) are formed in these cases.[97]

**Reactions of cyclopropenecarboxylate esters in the presence of other metals.** Apart from copper compounds the action of other metals, in particular, Ag, Pt,[110] Fe,[32] Rh,[16] on cyclopropene-3-carboxylate esters has been studied. Thus, in the presence of $AgClO_4$ (40 °C) or $AgBF_4$ (80 °C) or $PtO_2$ (220 °C), 1,2-dialkylcyclopropene-3-carboxylate esters (LXXVI) are converted to the dienoate esters (LXXVII).[110] It was proposed[110] that formation of (LXXVII) occurs via a vinylcarbene intermediate (LXXVIII), although the concerted mechanism proposed for copper compounds cannot be ruled out in this case.

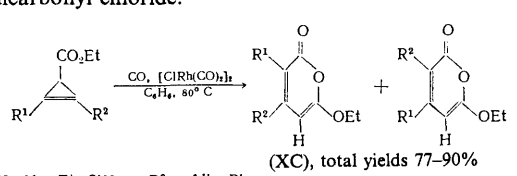



$R^1$, $R^2$ = H, Alk.

However, when chlorine or bromine at an α-position relative to the double bond is present in the side chain of a cyclopropene esters, ring-opening does not occur on treatment with $AgClO_4$ in MeOH but nucleophilic substitution takes place to give esters (LXXIX).[111,112]




It was recently demonstrated that α-pyrones can be obtained by carbonylation of cyclopropene-3-carboxylate esters in the presence of rhodium dicarbonyl chloride:[16]




$R^1$ = H, Me, Et, $SiMe_3$; $R^2$ = Alk, Ph.

In most cases the reaction is stereospecific, only isomer (XC) being formed, which makes this reaction valuable for preparative synthesis.

Other metal compounds—$Ni(COD)_2$, $MoCl_2-AlEt_3$, $WCl_5-SnMe_4$, a Ziegler–Natta catalyst—only cause cyclopropene esters (LX) to oligomerise.[70]

- - - o 0 o - - -

Thus, the material reviewed here demonstrates the availability of cyclopropene-3-carboxylate esters and their ability to undergo different chemical reactions with high conversion rates and selectivity. This makes it vital to carry out studies on the use of the reactions of cyclopropene-3-carboxylate esters and compounds derived from them in the directed organic synthesis of compounds with various useful properties.

## References


1. I A D'yakonov, M M Komendantov *Vestn. Leningr. Univ., Fiz. Khim.*, 1956, **4**(22) 166
2. R Breslow, D Chipman *Chem. Ind. (London)*, 1960, 1105
3. R Breslow, R Winter, M Battiste *J. Org. Chem.*, 1959, **24** 415
4. R Breslow, J Lockhart, A Small *J. Am. Chem. Soc.*, 1962, **84** 2793
5. I E Dolgii, G P Okonnishnikova, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1970, 197
6. O M Nefedov, I E Dolgii, G P Okonnishnikova, et al. *Angew. Chem.*, 1972, **84** 946
7. E A Shapiro, I E Dolgii, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 2096
8. N Petiniot, A J Anciaux, A F Noels, et al. *Tetrahedron Lett.*, 1978, 1239
9. G L Closs *Advances in Alicyclic Chemistry* (Edited by H Hart, G L Karabatsos), Vol. 1, Academic Press, New York–London, 1966, p. 53
10. T V Mandel'shtam *Sovremmenye Problemy Organicheskoi Khimii* (Current Problems in Organic Chemistry) (Edited by K A Ogloblin), Izd. LGU, Leningrad, 1976, p. 87
11. N S Zefirov, N V Averina, A M Boganov, et al. *Zh. Org. Khim.*, 1981, **17** 1450
12. A Demonceau, A F Noels, A J Anciaux, et al. *Bull. Soc. Chim. Belg.*, 1984, **98** 949
13. I N Domnin, E F Zhuraveleva, N V Pronina *Zh. Org. Khim.*, 1978, **14** 2323
14. P Dowd, P Garner, R Schapper *J. Org. Chem.*, 1982, **47** 4240
15. E A Shapiro, T N Romanova, I E Dolgii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2535
16. S H Cho, L S Liebeskind *J. Org. Chem.*, 1987, **52** 2631
17. I A D'yakonov, M I Komendantov *Zh. Obshch. Khim.*, 1961, **31** 3881
18. I A D'yakonov, M I Komendantov, S P Korshunov *Zh. Obshch. Khim.*, 1962, **32** 923
19. I A D'yakonov, M I Komendantov *Zh. Obshch. Khim.*, 1963, **33** 2448
20. F L Carter, V L Frampton *Chem. Rev.*, 1964, **64** 497
21. M I Komendantov, I A D'yakonov, I Gokhmanova, et al. *Zh. Org. Khim.*, 1965, **1** 209

22. M Vidal, M Vincens, P Arnaud *Bull. Soc. Chim. Fr.*, 1972, 657
23. E A Shapiro, G V Lun'kova, I E Dolgii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2529
24. E A Shapiro, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1977
25. USSR P. 566 830; *Byull. Izobret.*, 1977, (28)
26. I E Dolgii, G P Okonnishnikova, O M Nefedov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1979, 822
27. G P Okonnishnikova, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1978
28. E A Shapiro, G V Lun'kova, O M Nefedov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2535
29. E A Shapiro, G V Lun'kova, I E Dolgii, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1316
30. H Lind, A J Deutschmann, Jr. *Z. Org. Chem.*, 1967, **32** 326
31. I A D'yakonov, M I Komendantov, I G Gokhmanova *Zh. Obshch. Biol. Khim.*, 1959, **29** 3848
32. W A Donaldson, R P Hughes *J. Am. Chem. Soc.*, 1982, **104** 4846
33. W Kirmse, L Horner *Liebigs Ann. Chem.*, 1958, **614** 1
34. H Reimlinger *Chem. Ber.*, 1959, **92** 970
35. M Frank-Neumann, C Buchecker *Tetrahedron Lett.*, 1972, 937
36. M Frank-Neumann, C Dietrich-Buchecker *Tetrahedron Lett.*, 1976, 2069
37. D P Cox, I R Gould, N P Hacker, et al. *Tetrahedron Lett*, 1983, **24** 5313
38. C D DeBoer *J Chem. Soc., Chem. Commun.*, 1972, 377
39. M T H Liu *The Chemistry of Diazonium and Diazo Groups* (Edited by S Patai), John Wiley and Sons, London, 1978, p. 127
40. M I Komendantov, I N Domnin, R M Kenbaeva, et al. *Zh. Org. Khim.*, 1973, **9** 1420
41. I N Domnin, E F Zhuravleva, M I Komendantov, et al. *Zh. Org. Khim.*, 1977, **13** 1789
42. M J Jorgenson *J. Am. Chem. Soc.*, 1969, **91** 6432
43. U-J Vogelbacher, P Eisenbarth, M Regitz *Angew. Chem.*, 1984, **96** 691
44. D M DeSimone, P J Desrosiers, R P Hughes *J. Am. Chem. Soc.*, 1982, **104** 4842
45. C E Chidsey, A W Donaldson, R P Hughes, et al. *J. Am. Chem. Soc.*, 1979, **101** 233
46. J L Williams, D S Sgoutas, *J. Org. Chem.*, 1971, **36** 3064
47. M Vidal, M Vincens, P Arnaud *Bull. Soc. Chim. Fr.*, 1969, 4543
48. M Vidal, M Vincens, P Arnaud *Bull. Soc. Chim. Fr.*, 1972. 665
49. W A Donaldson, R P Hughes *Synth. Commun.*, 1981, **11** 999
50. G Maiere, M Hoppe, H P Reisenauer, et al. *Angew. Chem.*, 1982, **94** 445
51. I N Domnin, C Dumont, M Vincens, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1593
52. M Vidal, P Arnaud *Bull. Soc. Chim. Fr.*, 1972, 675
53. M Vincens, C Dumont, M Vidal *Tetrahedron*, 1983, **39** 4281
54. M Vincens, C Dumont, M Vidal *Tetrahedron*, 1981, **37** 2683
55. T N Grigorova *Sovremennye Problemy Organicheskoi Khimii* (Current Problems in Organic Chemistry) (Edited by K A Ogloblin), Izd. LGU, Leningrad, 1974, p. 100
56. T N Grigorova, M I Komendantov *Zh. Org. Khim.*, 1981, **17** 317
57. M Vincens, S Choubani, M Vidal *Tetrahedron Lett.*, 1981, **22** 4695
58. R Arnaud, S Choubani, R Subra, et al. *Can. J. Chem.*, 1985, **63** 2512
59. T N Grigorova, K A Ogloblin, M I Komendantov *Zh. Org. Khim.*, 1973, **9** 711
60. V R Kartashov, N V Gal'yanova, E V Skorobogatova, et al. *Zhur. Org. Khim.*, 1984, **20** 2623
61. V R Kartashov, N V Malisova, E V Skorobogatova, et al. *Zh. Org. Khim.*, 1986, **22** 867
62. R N Gymzina, I A D'yakonov, L P Danilkina *Zh. Org. Khim.*, 1970, **6** 2168
63. M Frank-Neumann, M Miesch *Tetrahedron Lett.*, 1982, 1409
64. Y Matsui, M Orchin *J. Organomet. Chem.*, 1983, **244** 369
65. T E Nalesnik, J G Fish, S W Hordon, et al. *J. Org. Chem.*, 1981, **46** 1987
66. W J Gensler, J J Langone, M B Floyd *J. Am. Chem. Soc.*, 1971, **93** 3828
67. I A D'yakonov, M I Komendantov *Zh. Obshch. Khim.*, 1963, **33** 2420
68. I A D'yakonov, V V Razin, M I Komendantov *Tetrahedron Lett.*, 1966, 1127
69. I A D'yakonov, V V Razin, M I Komendantov *Dokl. Akad. Nauk SSSR*, 1967, **177** 354
70. N Condé-Petiniot, A J Hubert, A F Noels, et al. *Bull. Soc. Chim. Belg.*, 1986, **95** 649
71. G V Lun'kova, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1982
72. C D DeBoer, D H Wadsworth, W C Perkins *J. Am. Chem. Soc.*, 1973, **95** 861
73. S Farid, K A Brown *J. Chem. Soc., Chem. Commun.*, 1976, 564
74. K A Brown-Wensley, S L Mattes, S Farid *J. Am. Chem. Soc.*, 1978, **100** 4162
75. J A Pincock, A A Montsokapas *Can. J. Chem.*, 1977, **55** 979
76. A Padwa *Acc. Chem. Res.*, 1979, **12** 310
77. M J Bennett, J T Purdham, S Takada, et al. *J. Am. Chem. Soc.*, 1971, **93** 4063
78. M I Komendantov, I N Domnin *Zh. Org. Khim.*, 1973, **9** 939
79. M L Deem *Synthesis*, 1982, 701
80. C Guiboret, R Danion-Buogot, D Danion, et al. *Tetrahedron Lett.*, 1981, **22** 441
81. M I Komendantov, R R Bekmukhametov *Zh. Org. Khim.*, 1971, **7** 423
82. M I Komendantov, R R Bekmukhametov, V G Novinskii *Zh. Org. Khim.*, 1976, **12** 801
83. W E von Doering, M Pomerantz *Tetrahedron Lett.*, 1964, 961
84. M A Battiste *Tetrahedron Lett.*, 1964, 3795
85. M L Deem *Synthesis*, 1972, 675
86. I E Dolgii, G P Okonnishnikova, E A Baidzhigitova *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1977, 2592
87. H-D Martin, L Kaudy, D Stusche *Tetrahedron Lett.*, 1977, 3561
88. N A Ampilogova, I A D'yakonov, R R Kostikov *Zh. Org. Khim.*, 1966, **2** 1898
89. M Vincens, C Dumont, M Vidal *Bull. Soc. Chim. France*, 1974, 2811
90. M Vincens, C Dumont, M Vidal *C. R. Seances Acad. Sci.*, 1978, **286** 717
91. I N Domnin, I A D'yakonov, M I Komendantov *Zh. Org. Khim.*, 1967, **3** 2076
92. H Prinzbach, U Fischer *Helv. Chim. Acta*, 1967, **50** 1669

93. L E Friedrich, R A Cormies *Tetrahedron Lett.*, 1971, 4761
94. J K Grandall, W W Conover *J. Org. Chem.*, 1978, **43** 1323
95. A A Frimer, A Antebi *J. Org. Chem.*, 1980, **45**, 2334
96. L Schrader *Tetrahedron Lett.*, 1971, 2993
97. M N Protopopova, Candidate's Thesis in Chemical Sciences, Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, 1986
98. E Wenkert, K J Chou, R P Hatch *Synth. Commun.*, 1977, **7** 375
99. I A D'yakonov, M I Komendantov, T S Smirnova *Zh. Org. Khim.*, 1969, **5** 1742
100. M I Komendantov, I N Domnin, E V Bulucheva *Tetrahedron*, 1975, **31** 2495
101. M Vincens, A Dussauge, M Vidal *Tetrahedron*, 1977, **33** 2936
102. I E Dolgii, Yu V Tomilov, O M Nefedeov, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 700
103. Yu V Tomilov, E A Shapiro, M N Protopopova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 631
104. P Binger, J McMeeking *Angew. Chem*, 1974, **86** 518
105. Yu V Tomilov, V G Bordakov, N M Tsvetkova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 336
106. E A Shapiro, M N Protopova, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 2153
107. M N Protopova, E A Shapiro, Yu V Tomilov, et al. *Izv. Akad Nauk SSSR, Ser. Khim.*, 1985, 2401
108. E A Shapiro, G V Lun'kova, M N Protopova, et al. *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2412
109. E A Shapiro, M N Protopopova, O M Nefedov *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 237
110. J H Leftin, E Gil-Av *Tetrahedron Lett.*, 1972, 3367
111. M Vidal, A Dussauge, M Vincens *Tetrahedron Lett.*, 1977, 313
112. R Arnaud, A Dussauge, R Faucher, et al. *Tetrahedron Lett.*, 1984, **40** 315